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Structure of Tetrabromobis(triphenylarsine)osmium(IV)

BY C. C. HINCKLEY* AND M. MATUSZ

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901, *USA*

AND P. D. ROBINSON

Department of Geology, Southern Illinois University, Carbondale, IL 62901, *USA*

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Abstract. $[\mathrm{OsBr_4\{As(C_6H_5)_3\}_2}]$, $M_r = 1122{\cdot}29$, monoclinic, $P2_1/n$, $a = 9{\cdot}435\ (2)$, $b = 21{\cdot}614\ (6)$, $c = 9{\cdot}793\ (2)$ Å, $\beta = 116{\cdot}78\ (2)^\circ$, $V = 1783\ (2)$ Å^3, $Z = 2$, $D_x = 2{\cdot}09$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 105{\cdot}03$ cm^{-1}, $F(000) = 1056$, $T = 295$ K, $R = 0{\cdot}041$ for 1733 unique observed reflections. Preparation by reflux of tetra-*n*-butylammonium hexabromoosmate(IV), triphenylarsine, and sodium acetate dihydrate dissolved in acetic acid and acetic anhydride. The central portion of the molecule is made up of an Os atom located on a center of symmetry and surrounded by four Br atoms in a square-planar conformation. Two *trans*-triphenylarsine groups are also coordinated to the Os. Bond distances involving Os are Os—As = 2·569 (1), Os—Br(1) = 2·451 (1) and Os—Br(2) = 2·472 (1) Å.

Experimental. Preparation by reaction of tetra-*n*-butylammonium hexabromoosmate(IV) (0·5 g, 0·43 mmol), triphenylarsine (0·5 g, 1·63 mmol), and sodium acetate dihydrate (0·5 g, 4·24 mmol) dissolved in 5 ml acetic acid and 5 ml acetic anhydride. Solution refluxed for 10 min, then cooled in an ice bath. Solid product filtered and washed with acetic acid and ethyl ether (yield, 0·3 g). Crystals appear black, yield deep purple–violet solutions in methylene chloride. Crystal used for data collection was 0·22 × 0·10 × 0·05 mm, black, bladed. Rigaku AFC5S diffractometer, graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scans, scan speed 6° min^{-1}, maximum of three scan repetitions to obtain $\sigma F/F < 0{\cdot}10$. Lattice parameters from least-squares fit of 25 reflections in 2θ range 6–21°. 3421 reflections measured (h −11 to 11, k 0 to 25, l 0 to 11); 3227 reflections unique, 1733 observed ($I > 3\sigma I$), $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}595$ Å^{-1}, $R_{\rm int} = 2{\cdot}4\%$ for 194 equivalent reflections. Three standard reflections ($\bar{1}\bar{1}4$, $\bar{1}14$, $\bar{1}21$) varied by 0·11, 0·41 and 0·00% respectively; no decay correction necessary. Data corrected for Lorentz, polarization and absorption (empirical ψ-scan method, four reflections, transmission range 0·67–1·0). Direct methods used to locate all non-H atomic sites. Full-matrix least-squares refinement of F magnitudes performed on 196 variables including all non-H positional and anisotropic thermal parameters and one scale factor. Phenyl-ring H atoms placed in geometrically correct positions (C—H = 0·95 Å) but not refined; H-atom B's fixed at $1{\cdot}2 \times B_{\rm eq}$ of associated C atom. Convergence yielded $R = 0{\cdot}041$, $wR = 0{\cdot}043$

Table 1. *Positional and equivalent isotropic thermal parameters for the non-*H *atoms and their e.s.d.'s*

$B_{\rm eq} = (8\pi^2/3)\ (U_{11} + U_{22} + U_{33} + 2U_{12}\cos\gamma + 2U_{13}\cos\beta + 2U_{23}\cos\alpha)$.

	x	y	z	$B_{\rm eq}$(Å^2)
Os	½	0	½	2·38 (3)
Br(1)	0·5332 (2)	0·01993 (6)	0·7592 (1)	3·45 (6)
Br(2)	0·2526 (2)	0·06151 (7)	0·3903 (2)	3·93 (6)
As	0·6721 (1)	0·09605 (6)	0·5303 (1)	2·74 (5)
C(1)	0·895 (1)	0·0903 (6)	0·676 (1)	3·0 (5)
C(2)	0·936 (2)	0·0724 (9)	0·827 (2)	5·7 (8)
C(3)	1·091 (2)	0·0708 (9)	0·937 (2)	6·1 (8)
C(4)	1·209 (2)	0·0863 (8)	0·902 (2)	5·9 (8)
C(5)	1·173 (2)	0·103 (1)	0·756 (2)	7 (1)
C(6)	1·016 (2)	0·1048 (7)	0·643 (2)	4·7 (7)
C(7)	0·679 (1)	0·1188 (6)	0·342 (1)	3·0 (5)
C(8)	0·752 (2)	0·0789 (7)	0·284 (1)	4·4 (6)
C(9)	0·747 (2)	0·0923 (9)	0·143 (2)	6·0 (9)
C(10)	0·673 (2)	0·143 (1)	0·061 (2)	7 (1)
C(11)	0·598 (2)	0·182 (1)	0·119 (2)	7 (1)
C(12)	0·601 (2)	0·1695 (8)	0·258 (2)	4·8 (7)
C(13)	0·619 (2)	0·1739 (6)	0·598 (2)	3·8 (6)
C(14)	0·718 (2)	0·2225 (9)	0·633 (3)	11 (1)
C(15)	0·683 (2)	0·278 (1)	0·685 (3)	13 (2)
C(16)	0·556 (2)	0·283 (1)	0·702 (2)	8 (1)
C(17)	0·462 (2)	0·236 (1)	0·679 (3)	8 (1)
C(18)	0·493 (2)	0·1802 (8)	0·628 (2)	6·4 (9)

Table 2. *Selected bond distances* (Å), *bond angles* (°) *and their e.s.d.'s*

Os–Br(1)	2·451 (1)	As–C(7)	1·93 (1)
Os–Br(2)	2·472 (1)	As–C(1)	1·94 (1)
Os–As	2·569 (1)	As–C(13)	1·95 (1)
Br(1)–Os–Br(2)	90·60 (5)	C(1)–As–C(13)	99·4 (5)
Br(1)–Os–As	87·66 (4)	C(7)–As–Os	112·7 (4)
Br(2)–Os–As	92·28 (5)	C(1)–As–Os	116·9 (4)
C(7)–As–C(1)	103·0 (5)	C(13)–As–Os	119·5 (4)
C(7)–As–C(13)	103·0 (6)		

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* Author to whom correspondence should be addressed.

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$[w = 1/\sigma^2(|F_o|)]$, $S = 1{\cdot}13$ and $(\Delta/\sigma)_{\max} = 0{\cdot}002$. A final difference Fourier synthesis showed $(\Delta\rho)_{\max} = 0{\cdot}89$, $(\Delta\rho)_{\min} = -0{\cdot}78$ e Å^{-3}. Minor disorder in ring C(13)—C(18) is indicated by slightly elevated temperature factors and two rather short C—C distances. Atomic scattering factors and anomalous-dispersion corrections from Cromer & Waber (1974). All computer programs from the *TEXSAN* crystal structure analysis package (Molecular Structure Corporation, 1985). Table 1 presents atomic coordinates and B_{eq} temperature factors while Table 2* lists selected interatomic distances and angles. Fig. 1 illustrates the molecular configuration, the thermal motion and the atom-numbering scheme.

Related literature. While other Os—As bonds have been reported and characterized (Bottomley, Lin & White, 1978), this compound is apparently the first triphenylarsine-containing Os complex to have been structurally characterized.

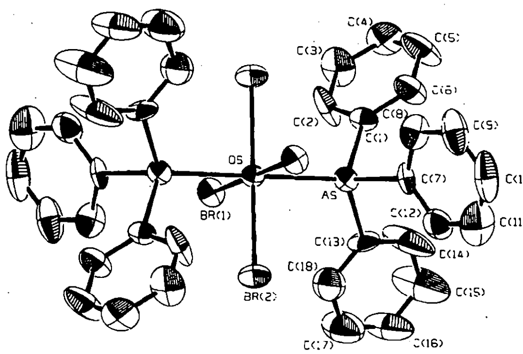

Fig. 1. Molecular structure and numbering scheme; thermal ellipsoids shown at the 50% probability level.

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* Lists of structure factors, anisotropic thermal parameters, distances and angles involving the phenyl rings, H-atom coordinates, and selected least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44446 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Tetramethylammonium Cerium(III) Bis(sulfate) Trihydrate

BY IVAN LEBAN, ANDREJ ARHAR, VERA JORDANOVSKA AND LJUBO GOLIČ

Department of Chemistry and Chemical Technology, E. Kardelj University, PO Box 537, 61001 Ljubljana, Yugoslavia

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Abstract. $(C_4H_{12}N)Ce(SO_4)_2.3H_2O$, $M_r = 460{\cdot}44$, orthorhombic, $Pca2_1$, $a = 11{\cdot}670\,(2)$, $b = 5{\cdot}440\,(1)$, $c = 21{\cdot}841\,(3)$ Å, $V = 1386\,(2)$ Å^3, $Z = 4$, $D_m = 2{\cdot}22\,(5)$, $D_x = 2{\cdot}206$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 36{\cdot}7$ mm^{-1}, $F(000) = 880$, $T = 293\,(1)$ K, final $R = 0{\cdot}030$ for 2034 observed reflexions. The Ce atom is coordinated by eight O atoms (five from sulfate groups, three from water molecules) in the form of an irregular polyhedron. The Ce—O distances range from 2·361 (5) to 2·593 (4) Å. The $N(CH_3)_4^+$ cation has the usual tetrahedral shape. The structure can be described as layers of $N(CH_3)_4$ cations, SO_4 anions, Ce and water molecules, SO_4 anions, $N(CH_3)_4$ cations, ...

Experimental. Single crystals prepared by slow evaporation of aqueous solution containing equivalent quantities of tetramethylammonium sulfate and cerium(III) sulfate. Colourless prismatic crystals with well developed {100}, {010} and {001} faces were obtained. D_m measured by flotation (mixture of diiodomethane and toluene). Crystal size 0·33 × 0·25 × 0·28 mm. Lattice parameters were determined by least-squares fit of θ values of 60 reflexions ($10 < \theta < 14°$); Enraf–Nonius CAD-4 diffractometer; data collected using $\omega/2\theta$ scans; $[(\sin\theta)/\lambda]_{\max} = 0{\cdot}70$ Å^{-1}; variable scan rate (min. 1·68, max. 20·1° min^{-1}), scan time 40 s, scan width (2θ) (0·6 +

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